IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Art Unit	: 1752	**Customer No.: 035811**
Examiner	: Barbara Lee Gilliam	
Serial No.	: 09/890,926	
Filed	: August 7, 2001	
Inventors	: Shinji Tanaka	Docket No.: 1265-01
	: Katsuhiro Uehara	
Title	: PHOTOSENSITIVE RESIN PRINT PLATE	Confirmation No.: 1861
	: MATERIAL AND PRODUCTION METHOD	
	: FOR PHOTOSENSITIVE RESIN PRINT PLATE	
		Dated: December 2, 2004

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Certificate of Mailing Under 37 CFR 1.8

For

Postcard
Claim for Priority Under 35 U.S.C. §119
English Translation of JP 11/350793

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Date: 2 Dec 2004

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Sir:

We submit herewith the English translation of Japanese Patent Application No. 11/350793, filed December 9, 1999, the priority of which is hereby claimed.

Respectfully submitted,

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[Pocket number] 55A00790-A

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[List of the documents submitted]

[Title of the document] Specification 1

[Title of the document] Abstract 1

[Necessity of proof] Required

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[Title of the document] Specification 1

[Title of the document] Abstract 1

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[Title of the document] Specification

[Title of the invention] Photosensitive resin printing plate material, and production method for photosensitive resin printing plate with relief thereon

[Claims]

[Claim 1] A photosensitive resin printing plate material, which comprises a support, a photosensitive resin layer, a photothermal-transforming substance layer, and a thermal coloring layer.

[Claim 2] A photosensitive resin printing plate material, as claimed in claim 1, wherein the photothermal-transforming substance layer is a layer having at least one dye selected from cyanine dyes, polymethine dyes and naphthalocyanine dyes.

[Claim 3] A photosensitive resin printing plate material, as claimed in claim 1 or 2, wherein the thermal coloring layer is UV-transmissive before heated, and is colored, after heated, to be substantially UV-non-transmissive.

[Claim 4] A photosensitive resin printing plate material, as claimed in claim 3, wherein the thermal coloring layer contains at least a thermal color former and a developer.

[Claim 5] A photosensitive resin printing plate material, as claimed in any of claims 1 through 4, wherein the photosensitive resin layer is a layer that can be photocured when exposed to light having a wavelength of 300 to 450 nm, and its thickness falls between 0.1 mm and 10 mm.

[Claim 6] A photosensitive resin printing plate material, as claimed in any of claims 1 through 5, which has a protective film on it.

[Claim 7] A method for producing a photosensitive resin printing plate with relief thereon, comprising a step of forming an image in a thermal coloring layer, a step of exposing a photosensitive

resin layer to light through the thermal coloring layer, and a step of developing the photosensitive resin layer.

[Detailed description of the invention]

The present invention relates to a photosensitive resin printing plate material capable of forming a photosensitive resin printing plate with relief thereon, and to a method for producing such a photosensitive resin printing plate from the material. The photosensitive resin printing plate thus obtained is usable as a relief printing plate or flexographic printing plate.

[0002]

[Prior art]

It is generally practiced to use photosensitive resin compositions as printing plate materials, and this practice prevails in the respective fields of relief printing, planographic printing, copperplate printing and flexographic printing.

[0003]

These printing plate materials are used as follows. A negative or positive original film is kept in contact with a photosensitive resin layer that is then irradiated with active light through the original film, to form a solvent-soluble area and a solvent-insoluble area in the photosensitive resin layer, for forming a relief image.

[0004]

A printing plate material needs a negative or positive original film and also a developing step. So, making one printing plate material involves many steps and much labor.

[0005]

At present, with the progress of computers, proposed are methods in which computer-processed information is directly delivered onto a printing plate material, to obtain a printing plate

material to be used for relief printing or flexographic plating without requiring the step of preparing an original film.

[0006]

Particularly proposed methods include (1) methods in which a toner or liquid ink is used to form an image on a photosensitive resin layer or on a thin film formed on the photosensitive resin layer (JP58-20029B, JP3-110164A, JP10-10709A, JP10-10710A, etc.), (2) methods in which a porous material or photosensitive layer is irradiated with a laser beam, and the irradiated area is molten or sublimed for directly obtaining a printing plate (JP52-56601A, JP53-127005A, JP56-40033B, JP61-106249A, JP7-505840T2, JP7-506780T2, JP8-99478A, JP8-90947A, JP9-142050A, JP9-254351A, etc.), and (3) methods in which an infrared sensitive layer is formed on the surface of a photosensitive resin layer and irradiated with a laser beam for forming a pattern without the necessity of using an original film (JP58-52646A, Japanese Patent 2773847, Japanese Patent 2773981, JP10-509254T2, JP8-305007A, JP8-305030A, JP9-171247A, JP9-166875A, JP10-39512A, JP10-39512A, JP10-73917A, etc.).

[0007]

Methods (1) have a problem that since a toner or liquid ink is used for forming an image, a fine image cannot be formed. Methods (2) have a problem that since a porous material or photosensitive layer is irradiated with a laser beam with high energy, it is difficult to obtain a sharp image, partly since the relief edges of the porous material or photosensitive layer are molten. Methods (3) have a problem that since the infrared sensitive layer is opaque, it is difficult to inspect the photosensitive resin plate material and another problem that even if it is transparent, a sufficient effect of ultraviolet shielding cannot be exhibited.

[0008]

[Problems to be solved by the invention]

In view of the above-mentioned problems, the present invention proposes a photosensitive resin printing plate material that is transparent enough to allow visual inspection, can be irradiated with a laser beam for forming an image different between an UV-transmissive area and a UV-non-transmissive area on the photosensitive resin printing plate material, and allows fine relief to be reproduced.

[0009]

[Means for solving the problems]

To solve the above-mentioned problems, the photosensitive resin printing plate material of this invention mainly has the following constitution: "A photosensitive resin printing plate material comprising a photosensitive resin layer, a photothermal-transforming substance layer, and a thermal coloring layer in this order on a support."

[0010]

Furthermore, the method for producing a photosensitive resin printing plate with relief thereon of this invention mainly has the following constitution: "A method for producing a photosensitive resin printing plate with relief thereon, comprising at least a step of forming an image in a thermal coloring layer, a step of exposing a photosensitive resin layer to light through the thermal coloring layer, and a step of developing the photosensitive resin layer."

[0011]

[Modes for carrying out the invention]

The modes for carrying out this invention are described below.

[0012]

The photosensitive resin printing plate material of this invention comprises a support, a photosensitive resin layer, a photothermal-transforming substance layer, and a thermal coloring layer.

[0013]

The respective layers are described below in detail.

[0014]

The support in this invention refers to a metal such as steel, stainless steel or aluminum, a plastic sheet made of a polyester, etc., or a synthetic rubber sheet made of styrene-butadiene rubber, etc.

[0015]

The photosensitive resin layer in this invention refers to a layer that can be photocured when irradiated with light, and preferably refers to a layer that can be photocured when exposed to light having a wavelength of 300 to 450 nm. The photosensitive resin layer is obtained by forming a photosensitive resin composition into a 0.1 to 10 mm sheet.

[0016]

The photosensitive resin composition generally contains at least an ethylenic unsaturated monomer and a photopolymerization initiator.

[0017]

The ethylenic unsaturated monomer is a substance that can be crosslinked by radical polymerization, and is not especially limited if it can be crosslinked by radical polymerization. Generally the following compounds can be enumerated: (meth)acrylates with a hydroxyl group such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate, and

β-hydroxy-β'-(meth)acryloyloxyethyl phthalate, alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, isoamyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, and stearyl (meth)acrylate, cycloalkyl (meth)acrylates such as cyclohexyl (meth)acrylate, halogenated alkyl (meth)acrylates such as chloroethyl (meth)acrylate, and chloropropyl (meth)acrylate, alkoxyalkyl (meth)acrylates such as methoxyethyl (meth)acrylate, ethoxyethyl (meth)acrylate, and butoxyethyl (meth)acrylate, phenoxyalkyl (meth)acrylates such as phenoxyethyl acrylate, and nonylphenoxyethyl (meth)acrylate, alkoxy alkylene glycol (meth)acrylates such as ethoxy diethylene glycol (meth)acrylate, methoxy triethylene glycol (meth)acrylate, and methoxy dipropylene glycol (meth)acrylate, (meth)acrylamides such as (meth)acrylamide, diacetone (meth)acrylamide, and N,N'-methylenebis (meth)acrylamide, compounds having only one ethylenic unsaturated bond, for example, 2,2-dimethylaminoethyl (meth)acrylate, 2,2-diethylaminoethyl (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylamide, N,N-dimethylaminopropyl (meth)acrylamide, 2-hydroxyethyl (meth)acrylate, and 3-chloro-2-hydroxypropyl (meth)acrylate, compounds having two or more ethylenic unsaturated bonds, for example, polyethylene glycol di(meth)acrylates such as diethylene glycol di(meth)acrylate, polypropylene glycol di(meth)acrylates such as dipropylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, glycerol tri(meth)acrylate, poly(meth)acrylates obtained by addition-reacting a compound having an ethylenic unsaturated bond and active hydrogen such as an unsaturated carboxylic acid or unsaturated alcohol with ethylene

glycol diglycidyl ether, poly(meth)acrylates obtained by addition-reacting an unsaturated epoxy compound such as glycidyl (meth)acrylate and a compound having active hydrogen such as a carboxylic acid or amine, poly(meth)acrylamides such as methylenebis(meth)acrylamide, polyvinyl compounds such as divinylbenzene, etc.

[0018]

The photopolymerization initiator is not especially limited, if it allows polymerizable carbon-carbon unsaturated groups to be polymerized by light. Above all, a photopolymerization initiator capable of producing radicals by the self decomposition or hydrogen extraction based on photo-absorption can be preferably used. Examples of if include benzoin alkyl ethers, benzophenones, anthraquinones, benzyls, acetophenones, diacetyls, etc.

[0019]

It is preferred to add a carrier resin to the photosensitive resin composition in this invention, in order to keep the form of the composition in a solid state. The carrier resin is generally selectively used in relation with the ink used. For obtaining a printing plate material suitable for using an aqueous ink, a general purpose rubber or elastomer such as butadiene rubber, nitrile rubber, urethane rubber, isoprene rubber, styrene butadiene rubber or styrene isoprene rubber can be used as the carrier resin. For obtaining a printing plate suitable for using an oily ink, a hydrophilic resin such as a water soluble polyamide resin or partially saponified polyvinyl acetate can be used.

[0020]

The following ingredients can also be added additionally. As a compatibilizing agent for enhancing compatibility and flexibility, it is possible to add a polyhydric alcohol such as ethylene glycol,

diethylene glycol, triethylene glycol, glycerol, trimethylolpropane or trimethylolethane, or a liquid rubber such as liquid polybutadiene or liquid polyisoprene. For enhancing thermal stability, a publicly known conventional polymerization inhibitor can be added. Preferred examples of the polymerization inhibitor include phenols, hydroquinones, catechols, etc. Furthermore, a dye, pigment, surfactant, ultraviolet light absorber, perfume, antioxidant, etc. can also be added.

[0021]

A method for obtaining the photosensitive resin layer from the photosensitive resin composition containing the carrier resin is described below. The carrier resin is dissolved into a solvent capable of dissolving the resin, and an ethylenic unsaturated monomer and a photopolymerization initiator are added. Subsequently, the mixture is sufficiently stirred to obtain a photosensitive resin composition solution, and the solvent is removed from the solution. The residue is then melt-extruded onto a support coated with an adhesive.

[0022]

The photothermal-transforming substance layer in this invention refers to a layer capable of generating heat when irradiated with a laser beam. For this reason, it contains a compound capable of absorbing a laser beam for generating heat.

[0023]

As examples of the compound capable of absorbing a laser beam for generating heat, enumerated are black pigments such as carbon black, titanium black, aniline black, and cyanine black, green pigments such as phthalocyanine and naphthalocyanine pigments, carbon graphite, diamine-based metal complexes, dithiol-based metal complexes, phenol thiol-based metal complexes,

mercaptophenol-based metal complexes, crystal water-containing inorganic compounds, copper sulfate, chromium sulfide, silicate compounds, metal oxides such as titanium oxide, vanadium oxide, manganese oxide, iron oxide, cobalt oxide, and tungsten oxide, hydroxides and sulfates of these metals, etc.

[0024]

Among them, as the compound capable of absorbing a laser beam for generating heat, it is preferred to use a dyestuff, especially dye capable of absorbing infrared light or near infrared light in view of the transmittance of light with a wavelength of 300 nm to 450 nm and transparency. Especially preferred dyestuffs include disperse dyestuffs based on cyanine, phthalocyanine, naphthalocyanine, dithiol metal complexes, azulenium, squalilium, croconium, and azo, metal complex dyes based on bisazo, bisazostylbene, naphthoquinone, anthraquinone, perylene, polymethine, and indoaniline, dyestuffs, especially dyes based on intermolecular CT, benzothiopyran, spiropyran, nigrosine, thioindigo, nitroso, quinoline, and fulgide, etc.

[0025]

Among them, cyanine dyes, polymethine dyes and naphthalocyanine dyes are especially preferred in view of laser beam absorptivity.

[0026]

It is preferred that the content of the compound capable of absorbing a laser beam for generating heat is from 1 to 40 wt% based on the weight of the solid matter in the photothermal-transforming substance layer composition. A more preferred range is from 5 to 25 wt%. If the content is 1 wt% or more, the laser beam can be efficiently absorbed, and if it is 40 wt% or less, the physical properties of the photothermal-transforming substance layer

composition are not adversely affected.

[0027]

The photothermal-transforming layer composition usually contains a carrier resin. The resin used is not especially limited. As examples of the resin, enumerated are polyvinyl alcohol, polyvinyl acetate, partially saponified polyvinyl acetate, cellulose resin, acrylic resin, polyvinyl pyrrolidone, nylon resins, urethane resins, ethylene vinyl acetate copolymer, polybutadiene, polyisoprene, styrene butadiene rubber, and nitrile rubber, though not limited to them.

[0028]

It is preferred that the amount of the carrier resin is from 20 to 99 wt% based on the weight of the photothermal-transforming substance layer composition. A more preferred range is from 30 to 60 wt%. If the amount is 20 wt% or more, the form of the photothermal-transforming layer can be kept, and if it is 99 wt% or less, the photothermal-transforming efficiency of the layer is not adversely affected.

[0029]

As another ingredient, a plasticizer can be added as required. As examples of the plasticizer, enumerated are glycols such as ethylene glycol, diethylene glycol, and triethylene glycol, polyalkylene glycols such as polyethylene glycol, and polypropylene glycol, liquid rubbers such as liquid polybutadiene, and liquid isoprene rubber, etc.

[0030]

The thickness of the photothermal-transforming substance layer is not especially limited, if it has a sufficient function of generating heat. A preferred range is from 0.1 μm to 30 μm.

[0031]

The thermal coloring layer of this invention refers to a layer that is UV-transmissive before it is heated and is colored, being substantially UV-non-transmissive if it is heated. The layer is not especially limited if it has the above-mentioned function. It is known that the layer is usually made to have the function by containing a color former and a developer. If substances described in JP61-121875A, JP1-99873A and JP5-104859A are, for example, used, the layer can have the function.

[0032]

Whether or not a substance is UV-transmissive can be expressed by an optical density. The optical density is generally expressed by D, and defined by the following equation.

$D = \log_{10} O = \log_{10}(1/\%) = \log_{10}({}_0/I)$

where $O = I_0/I$ is photographic density; T is transmittance; I_0 is the incident light intensity prevailing when the transmittance is measured; and I is the transmitted light intensity.

[0033]

In the measurement of optical density, it is known that the optical density can be calculated based on the measurement of transmitted light intensity or based on the measurement of incident light intensity. The optical density in this invention refers to a value calculated based on the transmitted light intensity.

[0034]

The optical density can be measured, for example, using an orthochromatic filter and Macbeth transmission densitometer "TR-927" (produced by Kollmorgen Instruments Corporation).

[0035]

In this patent, being UV-transmissive means that the optical density is 0.5 or less, and being substantially UV-non-transmissive means that the optical density is 1.5 or more.

[0036]

As the color former, a publicly known conventional color former can be used. For example, preferred are leuco compounds based on triphenylmethanephthalide, triallylmethane, phenothiazine, thiofluoran, xanthene, indophthalyl, spiropyran, azaphthalide, chromenopyrazole, methine, rhodamine anilinolactam, rhodamine lactam, quinazoline, diazoxanthene, bis-lactone, etc.

[0037]

As examples of the developer, enumerated are phenolic compounds, thiophenolic compounds, thiourea derivatives, organic acids and their metal salts, dibasic acids, organic phosphoric acid compounds, etc.

[0038]

Usually for fixing the color former and the developer, a carrier resin is mixed. The carrier resin is not especially limited. As particular examples of the carrier resin , enumerated are polyvinyl alcohol, polyvinyl acetate, partially saponified polyvinyl acetate, cellulose resin, acrylic resin, polyvinyl pyrrolidone, nylon resins, urethane resins, ethylene vinyl acetate copolymer, polybutadiene, polyisoprene, styrene butadiene rubber, and nitrile rubber, though not limited to them. Furthermore, as required, a plasticizer, a color formation preventive and so on can also be added.

[0039]

The thickness of the thermal coloring layer is not especially limited, if it is colored for substantially preventing the transmission of ultraviolet light. A preferred range is from 0.1 μm to 30 μm. A thickness of 0.1 μm or more is preferred, since the function of preventing the transmission of ultraviolet light can be exhibited, and a thickness of 30 μm or less is preferred, since

the absorption of ultraviolet light by a binder resin can be kept low.

[0040]

In this invention, as required, a protective film can be formed on the uppermost layer. The protective film can be a film of polyethylene terephthalate, polybutylene terephthalate, polyethylene or polypropylene, etc. It is preferred that the thickness of the film is from 30 μm to 150 μm. A thickness of 30 μm or more is preferred, since the film can serve as a protective film, and a thickness of 150 μm or less is preferred, since the protective film can be easily removed when it should be removed.

[0041]

Furthermore, as required, a mass transfer preventive layer can be formed between the photosensitive resin layer and another layer. This is provided for preventing that the compound capable of absorbing a laser beam for generating heat, color former and developer respectively contained in the photothermal-transforming substance layer and the thermal coloring layer migrate into the photosensitive resin layer. The material is not especially limited, if it can prevent the migration of them into the photosensitive resin layer. As examples of the material, enumerated are polyvinyl alcohol, polyvinyl acetate, partially saponified polyvinyl acetate, cellulose resin, acrylic resin, polyvinyl pyrrolidone, nylon resins, urethane resins, ethylene vinyl acetate copolymer, polybutadiene, polyisoprene, styrene butadiene rubber, nitrile rubber, polyester resins, polyethylene terephthalate, polypropylene, and polyethylene, though not limited to them.

[0042]

The order for laminating the support, the photosensitive resin layer, the photothermal-transforming substance layer, and

the thermal coloring layer is not especially limited. In view of processing, preferred is a printing plate material in which the support, the photosensitive resin layer, the photothermal-transforming substance layer, and the thermal coloring layer are laminated in this order, or in which the support, the photosensitive resin layer, the thermal coloring layer, and the photothermal-transforming substance layer are laminated in this order.

[0043]

A method for producing photosensitive resin printing plate material is described below. The photosensitive resin layer formed on the support is coated with a solution with the photothermal-transforming substance layer composition dissolved in a solvent, using a bar coater, slit die coater, gravure coater, comma coater, or reverse coater, etc., and the coating is dried. Subsequently it is coated with a solution with the thermal coloring layer composition dissolved in a solvent, and the coating is dried to obtain a photosensitive resin printing plate material. Furthermore, in the case where a protective film is used, the protective film can be coated with the thermal coloring layer and the photothermal-transforming substance layer in this order to achieve a necessary thicknesses using any of said coaters, being followed by drying, and the laminate can be brought into contact with the photosensitive resin layer formed on the support, using a roller, for obtaining a photosensitive resin printing plate material.

[0044]

From the photosensitive resin printing plate material obtained as described above, a photosensitive resin printing plate with relief thereon can be made as described below.

[0045]

The method for producing a photosensitive resin printing plate with relief thereon of this invention is described below.

[0046]

The method for producing a photosensitive resin printing plate with relief thereon of this invention comprises at least a step of forming an image in a thermal coloring layer, a step of exposing a photosensitive resin layer through the image, and a step of developing the photosensitive resin layer.

[0047]

The step of forming an image in a thermal coloring layer refers to a step in which the thermal coloring layer is image-wise irradiated with a laser beam through a protective film or after removing the protective film. The laser beam is absorbed by the photothermal-transforming substance layer that becomes hot in the area irradiated with the laser beam. As a result, the thermal coloring layer forms a color only in the heated area, and the colored area becomes substantially UV-non-transmissive. Thus, an image having the colored area and the non-colored area is formed in the thermal coloring layer. For laser beam irradiation, an ordinary laser beam source can be used. As the light source, any of various lasers such as Ar ion laser, Kr ion laser, He-Ne laser, He-Cd laser, ruby laser, glass laser, semiconductor laser, YAG laser, titanium sapphire laser, dye laser, nitrogen layer and metal vapor laser respectively with an oscillation wavelength in a range from 450 nm to 1500 nm can be used. Above all, a semiconductor layer is preferred, since it is reduced in size due to the technical progress in recent years and is economically more advantageous than other laser beam sources.

[0048]

The step of exposing a photosensitive resin layer through the thermal coloring layer refers to a step in which the photosensitive resin printing plate material irradiated with a laser beam by the above-mentioned method is fully irradiated with light usually having a wavelength of 300 nm to 450 nm through the thermal coloring layer having the image formed in it. Since the area with a color formed by laser irradiation is a substantially UV-non-transmissive area, the light having a wavelength of 300 nm to 450 nm does not reach the photosensitive resin layer in the area. Since irradiation light goes in also from the lateral sides of the photosensitive resin printing plate material, it is desirable to cover the lateral sides with a material incapable of transmitting the irradiation light. As an ordinary light source used for applying light having a wavelength of 300 nm to 450 nm, any of a high pressure mercury lamp, extra-high pressure mercury lamp, metal halide lamp, xenon lamp, carbon arc lamp, chemical lamp, and so on can be used. The photosensitive resin layer changes into a substance incapable of being dissolved and dispersed by a developer in the area irradiated with the irradiation light.

[0049]

In the step of developing the photosensitive resin layer, the printing plate material is installed in a brush type washing-out machine or spray type washing-out machine containing a developer capable of dissolving and dispersing the non-exposed area of the photosensitive resin layer, for development. The area irradiated with irradiation light remains to form a relief image.

[0050]

Thereafter, if necessary, the photosensitive resin printing plate material is dried and post-exposed and gets the adhesive removed. It can be used as a photosensitive resin printing plate

that can be installed in a printing machine.

[0051]

[Examples]

This invention is described below in detail in reference to examples. The respective layer compositions used in the examples, and their production methods are described below.

[0052]

(1) Photothermal-transforming substance layer composition

The following ingredients were mixed at room temperature to form a homogeneous solution.

(a) Polyvinyl pyrrolidone ("K-120" produced by ISP Japan) 40 parts by weight

(b) Polymethine-based dye ("Kayasorb" IR820(B) produced by Nippon Kayaku Co., Ltd.) 5 parts by weight

(c) Methyl ethyl ketone 250 parts by weight

(d) Methanol 100 parts by weight

(e) Methyl cellosolve 200 parts by weight

[0053]

(2) Thermal coloring layer composition

The following ingredients were mixed at room temperature to form a homogeneous solution.

(a) 3-(N-isoamyl-N-ethylamine)-7,8-benzfluoran 10 parts by weight

(b) Octadecylphosphonic acid 30 parts by weight

(c) Vinyl chloride vinyl acetate copolymer 30 parts by weight

(d) Toluene 135 parts by weight

(e) Methyl ethyl ketone 135 parts by weight

[0054]

(3) Photosensitive resin layer compositions

Photosensitive resin layer composition 1

Acrylonitrile was added to both the ends of polyethylene glycol with a number average molecular weight of 600, and it was hydrogen-reduced to obtain α,ω-diaminopolyoxyethylene. Sixty parts of an equimolar salt obtained from the α,ω-diaminopolyoxyethylene and adipic acid, 20 parts by weight of ε-caprolactam, and 20 parts by weight of an equimolar salt obtained from hexamethylenediamine and adipic acid were melt-polymerized under ordinary conditions, to obtain a polyamide 1 with a relative viscosity (measured at 25°C with 1 g of the polymer dissolved in 100 ml of chloral hydrate) of 2.50.

[0055]

The following ingredients were mixed to obtain photosensitive resin composition 1.

(a) Said polyamide 1 — 50 parts by weight

(b) Addition reaction product obtained from 1 mole of 1 mole of glycidyl methacrylate and 1 mole of acrylic acid, as an ethylenic unsaturated compound — 30 parts by weight

(c) Addition polymer obtained from 1 mole of propylene glycol diglycidyl ether and 2 moles of acrylic acid — 15 parts by weight

(d) Diethylene glycol — 5 parts by weight

(e) Dimethyl benzyl ketal — 1 part by weight

(f) Hydroquinone monomethyl ether — 0.01 part by weight

(g) Water — 30 parts by weight

(h) Ethanol — 70 parts by weight

[0056]

Photosensitive resin layer composition 2

One hundred parts by weight of water, 0.2 part by weight of sodium dodecylbenzenesulfonate, 3 parts by weight of

polyoxyethylene nonyl phenyl ether, 0.3 part by weight of potassium persulfate, 0.2 part by weight of t-dodecyl mercaptan, 29 parts by weight of methyl methacrylate, 1 part by weight of methacrylic acid, and 70 parts by weight of butadiene were made to react with each other as raw materials at 50°C for 20 hours, to obtain "water-dispersed latex rubber 1" with a solid content of 50.5 wt%, a number average particle size of 140 nm, and a glass transition temperature of -52°C.

[0057]

Sixty five parts by weight of water, 1.3 parts by weight of disproportionated potassium rhodinate, 1.7 parts by weight of potassium oleate, 1.5 parts by weight of sodium alkylsulfonate, 0.05 part by weight of t-dodecyl mercaptan, 0.1 part by weight of para-menthane hydroperoxide, 0.003 part by weight of iron sulfate, 0.006 part by weight of sodium ethylenediaminetetraacetate, 0.005 part by weight of sodium formaldehyde sulfoxylate, 1.2 parts by weight of potassium sulfate, and 100 parts by weight of butadiene were made to react with each other for polymerization at a low polymerization temperature of 5°C. The polymerization conversion rate was about 60%. "Water-dispersed latex rubber 2" with a solid content of 55 wt% and a number average particle size of 350 nm was obtained.

[0058]

The following ingredients were heated and mixed, and water was removed to obtain photosensitive resin composition 2.

[0059]

(a) Water-dispersed latex rubber 1

33.6 parts by weight (17 parts by weight as solid content)

(b) Water-dispersed latex rubber 2

14.5 parts by weight (8 parts by weight as solid content)

(c) Phenoxy polyethylene glycol acrylate

16 parts by weight

(d) Polycondensation product of glycerol polyether polyol, succinic anhydride and 2-hydroxyethyl acrylate

14 parts by weight

(e) Polybutadiene rubber ("Nipol" 1220L produced by Nippon Zeon Co., Ltd.) 20 parts by weight

(f) Nitrile rubber ("Nipol" 1042 produced by Nippon Zeon Co., Ltd.)

20 parts by weight

(g) Benzyl methyl ketal 1 part by weight

(h) Diocyl phthalate 2 parts by weight

(i) Hydroquinone monomethyl ether 0.1 part by weight

[0060]

Example 1

A 100 μm thick polyethylene terephthalate film used as a protective film was coated with said thermal coloring layer composition using a bar coater, and the coating was dried to form an 8 μm thick thermal coloring layer.

[0061]

The thermal coloring layer was coated with said photothermal-transforming substance layer composition using a bar coater, and the coating was dried to form a 2 μm thick photothermal-transforming substance layer. This film was sufficiently transparent and green and had an optical density of 0.4.

[0062]

Said photosensitive resin layer composition 1 was cast onto a 250 μm thick polyethylene terephthalate film coated with a polyester-based adhesive, used as a support, and the coating was dried at 60°C for 3 hours to form a photosensitive resin layer with

a dry thickness of 650 μm.

[0063]

Said film was pressed to and mounted on the film having the photosensitive resin layer in such a manner that the photosensitive resin layer and the photothermal-transforming substance layer faced each other, to obtain a photosensitive resin printing plate material.

[0064]

The photosensitive resin printing plate material obtained like this was installed in FX400-AP (platesetter produced by Toray Engineering Co., Ltd.) and image-wise irradiated with a semiconductor laser beam (wavelength 830 nm, beam diameter 20 μm) through the protective film at 800 mJ/cm^2, and an image could be formed in the thermal coloring layer. The optical density of the thermally colored area was 2.6.

[0065]

Subsequently an exposure machine having 10 chemical lamps (FL20SBL-360 produced by Mitsubishi Electric Corp.) emitting ultraviolet light was used for exposure through the thermal coloring layer at a distance of 60 mm for 2 minutes. The edges of the printing plate material were covered with a light-shielding film, for being shielded from irradiation.

[0066]

After completion of exposure, the protective film was removed, and a brush developing machine was used to develop for 1 minute using water of 25°C, and the non-crosslinked area of the photosensitive resin layer was washed out to obtain a photosensitive printing plate having a relief image formed. The obtained printing plate could be used as a relief printing plate.

[0067]

Example 2

As described for Example 1, a thermal coloring layer and a photothermal-transforming substance layer were formed in this order on a protective film.

[0068]

A press heated to 90°C was used to hold the photosensitive resin layer composition 2 between a 125 μm thick polyethylene terephthalate film coated with a polyester-based adhesive, used as a support, and said protective film having the thermal coloring layer and the photothermal-transforming substance layer laminated, to ensure that the thickness of the photosensitive layer became 1.7 mm, for obtaining a photosensitive resin printing plate material.

[0069]

The photosensitive resin printing plate material obtained like this was processed as described for Example 1, to form an image in the thermal coloring layer.

[0070]

Subsequently an exposure machine having 10 chemical lamps as used in Example 1 was used to expose, at first, from the support side for 2 minutes and then, through the thermal coloring layer for 5 minutes. The edges of the printing plate material were covered with a light shielding film, for being shielded from irradiation.

[0071]

After completion of exposure, the protective film was removed, and a brush developing machine was used to develop for 7 minutes using water of 40°C, and the non-crosslinked area of the photosensitive resin layer was washed out to obtain a photosensitive resin printing plate having a relief image formed. The printing plate could be used for flexographic printing.

[0072]

Example 3

A 100 μm thick polyethylene terephthalate film used as a protective film was coated with said photothermal-transforming substance layer composition using a bar coater, and the coating was dried to form a 2 μm thick photothermal-transforming substance layer.

[0073]

The photothermal-transforming substance layer was further coated with said thermal coloring layer composition using a bar coater, and the coating was dried to form an 8 μm thick thermal coloring layer. The film was sufficiently transparent and green, and had an optical density of 0.4.

[0074]

Subsequently said photosensitive resin layer composition 1 was cast onto a 250 μm thick polyethylene terephthalate film coated with a polyester-based adhesive, used as a support, and the coating was dried at 60°C for 3 hours, to obtain a photosensitive resin layer with a dry thickness of 650 μm.

[0075]

Said film was pressed to and mounted on the film having the photosensitive resin layer using a roller in such a manner that the photosensitive resin layer and the thermal coloring layer faced each other, to obtain a photosensitive resin printing plate material.

[0076]

The photosensitive resin printing plate material obtained like this was installed in FX400-AP (platesetter produced by Toray Engineering Co., Ltd.) and image-wise irradiated with a semiconductor laser beam (wavelength 830 nm, beam diameter 20 μm)

through the protective film at 800 mJ/cm^2, and an image could be formed in the thermal coloring layer. The optical density of the thermally colored area was 2.6.

[0077]

Subsequently an exposure machine having 10 chemical lamps as used in Example 1 was used to expose through the thermal coloring layer for 2 minutes at a distance of 60 nm. The edges of the printing plate material were covered with a light shielding film, for being shielded from irradiation.

[0078]

After completion of exposure, the protective film was removed, and a brush developing machine was used to develop for 1 minute using water of 25°C, and the non-crosslinked area of the photosensitive resin layer was washed out to obtain a photosensitive resin printing plate having a relief image formed. The printing plate could be used as a relief printing plate.

[0079]

Comparative Example 1

A photosensitive resin printing plate material was produced as described for Example 1, except that it did not have the photothermal-transforming substance layer.

[0080]

The photosensitive resin printing plate material was installed in FX400-AP (platesetter produced by Toray Engineering Co., Ltd.) and image-wise irradiated with a semiconductor laser beam (wavelength 830 nm, beam diameter 20 μm) through the protective film at 800 mJ/cm^2. No image could be formed in the thermal coloring layer.

[0081]

It is considered that since no photothermal-transforming

substance layer existed, the thermal coloring layer was not heated or colored.

[0082]

[Effect of the invention]

This invention provides a photosensitive resin printing plate material not requiring any original film, and allows a relief image to be formed.